

AD A088565

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

12 ARO 14069.4-MS

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
	AD-A088565	
4. TITLE (and Subtitle)	5. TYPE OF REPORT & PERIOD COVERED	
6 Directional Solidification of Nonoxide Eutectics	FINAL Dec. 1, 1976 - May 31, 1980	
7. AUTHOR(s)	8. CONTRACT OR GRANT NUMBER(s)	
Dr. V. S./Stubican Dr. R. C./Bradt	Grant Number DAAG-29-77-G-0057 DAAG-29-77-G-0050	
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS	
The Pennsylvania State University/ University Park, PA 16802	(11) 31 Jul 1980	
11. CONTROLLING OFFICE NAME AND ADDRESS	12. REPORT DATE	
U. S. Army Research Office Post Office Box 12211 Research Triangle Park, NC 27709	12 7	
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	13. NUMBER OF PAGES	
Office of Naval Research Carnegie-Mellon University Room 407, Margaret Morisson Bld. Pittsburgh, PA 15213	6	
16. DISTRIBUTION STATEMENT (of this Report)	15. SECURITY CLASS. (of this report)	
Approved for public release; distribution unlimited.	Unclassified	
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE	
NA	NA	
16. SUPPLEMENTARY NOTES		
The findings in this report are not to be construed as an official Department of the Army position, unless so designated by other authorized documents.		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)		
Silicon carbide, boron carbide, zirconium carbide, titanium carbide, titanium dioxide, Eutectic solidification, structure, microstructure, hardness, fracture toughness, wear.		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number)		
The directional solidification of the eutectic composition in the systems SiC-B ₄ C, TiC-TiB ₂ , ZrC-ZrB ₂ , and ZrC-TiB ₂ was studied. Microstructure, crystallography, hardness, fracture toughness and wear were determined. In several of the studied system mechanical properties exceeded that of the end members.		

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FINAL REPORT

"DIRECTIONAL SOLIDIFICATION OF NON-OXIDE EUTECTICS"

The directional solidification of the eutectic composition in the systems SiC-TiB_2 , TiC-TiB_2 , ZrC-ZrB_2 and ZrC-TiB_2 was studied. Microstructure, crystallography, hardness, fracture toughness and wear were determined. In several of studied systems mechanical properties exceeded that of the end members. The important findings are:

The $\text{SiC-B}_4\text{C}$ Eutectic

Directionally solidified $\text{SiC-B}_4\text{C}$ eutectic formed lamellar microstructures with no colonies if the solidification rate (R) was below 2cm/hr. It was determined that $\langle 001 \rangle$ of B_4C and $\langle 111 \rangle$ of SiC were parallel to the eutectic growth direction, and that the interlamellar spacing was proportional to the inverse square root of solidification rate. The minimum wear was found with compositions close to eutectic. At $R \approx 9$ cm/hr the most wear resistant specimens were obtained. $\text{SiC-B}_4\text{C}$ eutectic ingot solidified at approximately 9cm/hr had considerably better wear resistance than solidified B_4C or hot pressed SiC .

The ZrC-ZrB_2 Eutectic

(1) The microstructure consists of columnar grains of parallel lamellae whose interlamellar spacings range from 2.75 to 1.63 μm , corresponding to growth rates of 0.4 to 5.4 cm/hr.

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(2) The λ^2_R law holds for this system where:

$$\lambda^2_R = 9.32 \times 10^{-9} \text{ cm}^3/\text{hr}$$

(3) At λ values from 2.75 to 1.85 μm , the microstructure consists only of columnar grains of lamellae. At λ values less than 1.85 μm , the presence of misorientation and colonies is observed, the amount present increasing with smaller λ values, that is, as the growth rate increases.

(4) The disordered regions have been associated with one of two proposed phenomena:

(a) The misorientation and colonies arising from the constitutional supercooling effect at fast rates of growth affect the entire bulk of the body by imposing a strain field; or

(b) At $\lambda = 1.85 \mu\text{m}$, the phases approach coherency and a strain field develops, whereby the misorientation and colonies may be an effect rather than a cause,

(5) The mechanical properties of nearly all the directionally solidified eutectics are superior to those of the individual components,

(6) The microhardness demonstrates Hall-Petch behavior from $\lambda = 2.75$ to 1.85 μm ; it decreases for smaller λ values. The maximum hardness found is 2449 kg/mm^2 .

(7) The fracture toughness shows a maximum of 5.44 $\text{MN}/\text{m}^{3/2}$ at the λ value of 1.85 μm .

(8) The wear resistance is at a maximum at $\lambda = 1.85 \mu\text{m}$.

(9) The Evans and Wilshaw and Rabinowicz relationships between the wear volume and H^{-1} , $K_{Ic}^{-3/4}$, and $H^{-1/2} K_{Ic}^{-3/4}$ show consistent results for these data.

(10) The orientation relationships are:

Interfacial plane // $(111)_{ZrC}$ // $(00\cdot1)_{ZrB_2}$

Growth direction // $[01\bar{1}]_{ZrC}$ // $[01\cdot0]_{ZrB_2}$

The ZrC-TiB₂ Eutectic

(1) The microstructure consists of columnar grains of a Chinese script type of broken and deformed lamellae morphology. Solid solution between the two phases exists.

(2) The $\lambda^2 R$ law holds for this system where:

$$\lambda^2 R = 9.86 \times 10^{-8} \text{ cm}^3/\text{hr}$$

(3) The interlamellar spacing decreases consistently from 8.27 to 4.49 μm as the growth rate increases from 0.2 to 1.0 cm/hr at which point the microstructure breaks down and the alignment is lost.

(4) The mechanical properties of nearly all the directionally solidified eutectics are superior to those of the individual components.

(5) The microhardness shows Hall-Petch behavior until microstructural breakdown occurs. The maximum hardness obtained is 2165 kg/mm².

(6) The fracture toughness increases with decreasing λ . The maximum value of K_{Ic} is 2.85 MN/m^{3/2}.

(7) The wear resistance increases with decreasing λ .

(8) The orientation relationships are:

Interfacial plane // $(111)_{\text{ZrC}}$ // $(00\cdot1)_{\text{TiB}_2}$

Growth direction // $[001]_{\text{ZrC}}$ // $[01\cdot0]_{\text{TiB}_2}$

In summary, the directionally solidified eutectic ZrC-ZrB_2 should have a definite possibility for high strength, high temperature uses. Its mechanical properties are as high or higher than the best dense, hot-pressed ceramics, and its melting point is extremely high. These qualities, in conjunction with its low vaporization and absence of cracking, make it a potentially useful material.

The directionally solidified eutectic ZrC-TiB_2 is a mechanically inferior composite to the former. Its mechanical properties are consistently of lower value, and its heavy vaporization and extensive cracking indicate minimal potential for use.

The TiC-TiB_2 Eutectic

The directional solidification of the eutectic composition in the system TiC-TiB_2 was studied. Both the microstructural and crystallographic relationships between the two phases were investigated with the view to relate structure on a crystallographic and microscopic level to those parameters which control the form of the final ensemble. Indentation hardness and toughness and abrasive wear were observed as a function of the interlamellar spacing to extend the understanding of mechanical property behavior of in situ composite materials.

For the system which was investigated, the crystallographic relationship between the two phases can be summarized as:

- (1) The interfacial planes and growth directions have low Miller indices.
- (2) The difference in the spacing of ions on the titanium sublattice is negligible between the carbide and boride phases on the interfacial plane.
- (3) The interfacial planes contain only one kind of atom.
- (4) The form of the microstructure may be predicted from the volume fraction of minor phase as set out by Cooksey et al. (1964) by minimizing the surface energy.
- (5) The interlamellar spacing is a function of the inverse square root of the solidification rate.

Some mechanical properties of the TiC-TiB_2 directionally solidified eutectic were studied. It was concluded that:

- (6) Hardness increases with decreasing interlamellar spacing to a constant value which approaches that of the harder end member.
- (7) The fracture toughness exceeds that of either end member regardless of solidification rate, and is best described by a Hall-Petch type relationship.
- (8) The indentation toughness is affected by the orientation of the crack to the microstructure. The crack does not always originate from an apex of the indentation, nor does it always travel in a straight line.

(9) The wear behavior is controlled by the solidification rate. The more rapid the solidification rate, the more wear resistant the material. Only the most rapidly solidified eutectic was more wear resistant than hot pressed TiB_2 .

Personnel

Three graduate students, Mr. Ch Sorrell, Mr. H. Beratan and Mr. Jan der Hong worked on the project and all of them graduated with M.S. in Ceramic Science.

Thesis and Publications

1. Charles Sorrell, M.S. thesis "The Directional Solidification and Properties of the ZrC-SrB_2 and ZrC-TiB_2 Eutectics".
2. Howard Beratan, M.S. thesis "Directional Solidification and Properties of the TiC-TiB_2 Eutectic".
3. Jan der Hong, M.S. thesis "Directional Solidification of $\text{SiC-B}_4\text{C}$ Eutectic". Mat. Res. Bull. 14, 775 (1979).